Photosensitive Materials with Novel Phenolic Resins

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1. Introduction

Phenolic resin has been widely used as materials for mold resin, insulating materials, adhesives, or photoresist etc. in machinery, engineering, or semiconductor field, because of its excellent electrical insulation properties, acid resistance, heat resistance, water and fire resistance, with low cost [1]. On the other hand, phenolic resin has the disadvantage of fragility. Until now, in order to improve toughness of phenolic resin, various methods are applied, such as modification by drying oil, addition of natural rubber or NBR, reinforcement by grass fiber etc., but these methods were incompatible with heat resistance or moldability [1,2].

Recently, the protective film made from photosensitive phenolic resin compositions were also reported as an inter layer dielectrics, stress buffer layers, and alpha rays protections of semiconductor devices as a permanent film [3]. However, cured film from these phenolic resins could not be expected to have enough film properties as represented by elongation. Though, a thermal cycle test is known as an important reliability test of a semiconductor device, elongation is considered as the key parameter for this test. And also low temperature curable and having low stress are another issues to keep the device reliability good, especially with large size dies or thin wafer.

Then, we focus on the phenolic resins that having biphenyl unit. This report describes novel positive-type photosensitive materials with such phenolic resins having good film properties i.e. high elongation, low residual stress and high glass transition temperature with the low cure temperature at 250 °C or lower. Mechanical properties, heat resistance, residual stress, and thermal cycle test results of the film were also evaluated.

2. Experimental

2.1. Elongation measurement

Cresol novolac resin EP-4080G was purchased from Asahi Organic Chemicals Industry. Phenol-dicyclopentadienyl resin (P-DCPD) was purchased from Gun ei Chemical Industry. Phenol-salicylaldehyde resin MEH-7500, phenol-aralkyl resin MEH-7800M and phenol-biphenyl resin MEH-7851M were purchased from Meiwa Plastic Industries. These resins were dissolved in the gamma-butylactone (GBL), with crosslinking agent. And then each of them were filtered and coated on 6 inch silicon wafer and pre-baked at 120 oC for 3 minutes (Tokyo Electron Mark-8). The coated film with about 10 µm thick on a wafer was cured at 250 oC for 1 hour under N2 atmosphere, respectively. The elongation of cured film was measured with the testing machine , respectively (Orintec Tensilon UTM-II-20).

2.2. GPC measurement

0.02g of each polymer was added to 5mL N-methyl pyrrolidone. GPC measurement of each sample was performed with the analytical curve of standard polystyrene.
2.3. Geometry optimization

First, the chemical structure of the trimmer of each phenolic resin is drawn with ChemWindow (Bio-Rad Laboratories). In this case, it is supposed that the linkages are at the each ortho positions of phenolic hydroxyl group. Secondly, the structural formula of the drawn phenolic resin was copied to SymApps (Bio-Rad Laboratories), and the three-dimensional structure was calculated by the molecular mechanics method (MM2). And then, distance between OH groups of each was calculated.

2.3. Synthesis of phenolic resins

Synthetic scheme of phenolic resins are indicated in scheme 1. Phenol derivatives which have 2 or 3 hydroxyl groups and 4,4'-methoxy methyl biphenyl (BMMB) were dissolved into propylene glycol monoethyl ether mono acetate (PGMEA), and the solution was stirred under N₂ atmosphere. And then, p-toluene sulfonic acid was added to the solution and heated by oil bath to 120°C and stirred for 5hrs and poured into water as to make polymer frake. The polymer precipitate was filtrated and dried at 50°C for 72 hours under the vacuum. The polymerization of the target polymer was confirmed by GPC and NMR measurement.

![Scheme 1. Synthesis of phenolic resin having biphenyl unit.](image)

2.4. Preparation of photosensitive phenolic resin compositions

Photosensitive phenolic resin varnishes were prepared by adding the phenolic resins, photoactive compound (PAC), crosslinking agent and adhesion promoter, to GBL.

2.5. Lithography and observation of cured film

The photosensitive phenolic resin varnishes were coated on 6 inch silicon wafer and pre-baked at 120°C for 3 minutes (Mark-8). The coated film about 10 µm thick on a wafer was exposed through a patterning mask by i-line stepper (Nikon NSR2005i8A) with 200mJ / cm² to 800mJ / cm². The exposed film was developed with 2.38% tetramethylammonium hydroxide solution for 60 seconds and then rinsed with ion-exchanged water for 10 seconds (SOKUDO SC-W60A-AV9). The patterned film was cured and observed by optical microscope.

2.6. Thermal and mechanical properties

The films which were coated on 6 inch silicon wafers and cured at 200°C and 250°C for 1 hours under N₂ atmosphere, respectively. The residual stress of these samples was determined by thin film stress measurement system (KLA-Tencor FLX2320).

Glass-transition temperature (Tg) and coefficient of thermal expansion (CTE) of these films were determined by thermal mechanical analyzer (Shimadzu TMA-50), the temperature of 5% weight loss were determined by thermogravimetry analyzer (Shimadzu TGA-50), and the mechanical properties such as elongation, young’s modulus, and strength were measured by tensile test.

2.7. Thermal cycle test

Thermal cycle test of cured films were performed on the conditions of carrying out 1000 cycles by turns every chamber (-65°C and 135°C) for 30 minute cycle (Espec, Thermal cycle chamber TSE-11).

3. Results and discussion

3.1. Elongation of films using various phenolic resins

The result of elongation measurement of the cured films are shown in Fig. 1 with the data of each molecular weight of polymer and the distance between phenolic hydroxyl groups of each polymer estimated from the optimized structure. The cured film from varnish using
P-DCPD and MEH-7800M with a comparatively long distance between hydroxyl groups showed elongation higher than the one using novolac resin and MEH-7500, and the one using MEH-7851M which has especially long distance of 11.3 Å showed excellent elongation of 70%. This is because longer hydroxyl group distance, i.e., the longer distance between bridging points provides appropriate crosslink density by introducing a biphenyl unit.

3.2. Solubility to alkaline developer and pattern shape of cured film.

Photosensitive phenolic resin compositions prepared by aforementioned were investigated. The vanish using MEH-7851 shows far low solubility to alkaline developer compared with the one using EP-4080G because of the lower hydroxyl group density. The molecular weight of resin needed to be lowered in order to make development possible within an applicable time. It also became clear that 70µm pattern, comparatively big one, was buried after curring using MEH-7851M. This is considered because MEH-7851M had only the weak molecular interaction and the quite low softening point.

3.3. Performance of biphenyl resin using polyhydric phenol.

To solve the problem of solubility, we focused on the resins using resorcinol, pyrogallol, or phlorogluconol which has 2 or 3 hydroxyl groups in one molecular. It is considered that the interaction of resin is also enhanced by making the number of hydroxyl groups in one molecular increase. The increase in hydroxyl groups allows the molecular weight of resin to be higher and the softening point of resin to become still higher. As a result, both of polymers contains pyrogallol and phlorogluconol show high solubility, and after cured, even small pattern were not buried. Although the composition using catechol-biphenyl polymer did not show such a good effect from the point of solubility and polymer interaction. (Table 1). The cured film from these polymer also shows high elongation. After this section, the result of various properties are described about pyrogallol and phlorogluconol resins with the especially outstanding performance.

3.4. Film properties

Table 2 shows the summary of thermal resistance, mechanical properties and residual stress of the cured film from those compositions using pyrogallol-biphenyl or phlorogluconol-biphenyl resin. The elongation of each film shows high elongation even at 200°C cure. Tg of the film exceeded the cure temperature, because of the three-dimensional network of the cured film based on the reaction between polymer and crosslinking agent. The residual stress of the film cured at each temperature is low, thus these films can be used as the low-stress protective material.

Table 1. Property of cured film and solubility to alkaline developer

<table>
<thead>
<tr>
<th></th>
<th>EP-4080G</th>
<th>MEH-7851M</th>
<th>Catechol-biphenyl</th>
<th>Pyrogallol-biphenyl</th>
<th>Phlorogluconol-biphenyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Elongation [%]</td>
<td>4</td>
<td>70</td>
<td>40</td>
<td>30</td>
<td>25</td>
</tr>
<tr>
<td>Development rate [nm/s]</td>
<td>15</td>
<td>5</td>
<td>10</td>
<td>20</td>
<td>35</td>
</tr>
<tr>
<td>Buried pattern size of cured film [µm]</td>
<td>25</td>
<td>70</td>
<td>20</td>
<td>&lt;3</td>
<td>&lt;3</td>
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Table 2. Film properties with polyhydric phenol-biphenyl resin compositions.

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</thead>
<tbody>
<tr>
<td>Pyrogallol-biphenyl</td>
<td>200</td>
<td>60</td>
<td>290</td>
<td>45</td>
<td>45</td>
<td>100</td>
<td>3.5</td>
<td>315</td>
<td>10</td>
</tr>
<tr>
<td>Phlorogluconol-biphenyl</td>
<td>200</td>
<td>60</td>
<td>320</td>
<td>40</td>
<td>30</td>
<td>125</td>
<td>3.8</td>
<td>325</td>
<td>15</td>
</tr>
</tbody>
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3.5. Result of thermal cycle test

Table 3 shows the result of the thermal cycle test. “NG” means that crack happened after the thermal cycle test, “OK” means no crack at all even after the thermal cycle test.

<table>
<thead>
<tr>
<th>polymer</th>
<th>EP-4080G</th>
<th>Pyrogallol-biphenyl</th>
<th>Phenolurucinol-biphenyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>judge</td>
<td>NG</td>
<td>OK</td>
<td>OK</td>
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The crack did not arise on the cured film containing biphenyl unit. It is proved that the biphenyl unit provides the good reliability in the thermal cycle test with high elongation.

4. Conclusion

We report here the novel positive-type photosensitive composition using phenolic resin having biphenyl unit that has higher elongation. The phenolic resin composition consist of pyrogallol-biphenyl and phenolurucinol-biphenyl polymer showed high solubility to alkaline developer. The cured film had good shape, excellent thermal resistance, high mechanical properties, and low residual stress. And as thermal cycle test of these phenolic resin shows a capability for next generation protective layer of the semiconductor device which requires low temperature curable and low stress.

References